Electronic Supplementary Material for
Journal of Material Chemistry A

Air-Stable High-Efficiency Solar Cells with Dry-Transferred Single-Walled Carbon Nanotube Films

Kehang Cui, Anton S. Anisimov, Takaaki Chiba, Shunjiro Fujii, Hiromichi Kataura, Albert G. Nasibulin, Shohei Chiashi, Esko I. Kauppinen, and Shigeo Maruyama*

\* \textit{Department of Mechanical Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan. Fax: +81-80-3545-9236; Tel: +81-80-3545-9236; E-mail: maruyama@photon.t.u-tokyo.ac.jp}

\textit{Canatu Ltd., Konalankuja 5, FI-00390 Helsinki, Finland.}

\textit{Nan system Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8562, Japan.}

\textit{Department of Applied Physics, Aalto University School of Science, Aalto FI-00076, Finland.}

\textit{Skolkovo Institute of Science and Technology, 100 Novaya st., Skolkovo, Moscow Region, Russia 143025}

Corresponding Author:
Shigeo Maruyama, maruyama@photon.t.u-tokyo.ac.jp.
Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Tokyo, 113-8656, Japan; Tel: +81-3-5841-6421; Fax: +81-3-5800-6983.
S1. X-ray photoelectron spectroscopy of the Si substrate used in the SWNT/Si solar cell

X-ray photoelectron spectroscopy was employed to characterize the oxide thickness of the Si substrate used in the SWNT/Si solar cells. Figure S1 shows the Si 2p spectrum. The thickness of the oxide layer \( d_{\text{ox}} \) could be precisely calculated as

\[
d_{\text{ox}} = \lambda_{\text{ox}} \sin \theta \ln \left( \frac{I_{\text{ox}}}{\beta I_{\text{Si}}} + 1 \right)
\]

where \( \lambda_{\text{ox}} \) is the attenuation length of the Si 2p photoelectrons in SiO\(_2\), \( \theta \) is the photoelectron take-off angle, \( \beta \) is the Si 2p intensity ratio of infinitely thick SiO\(_2\) and Si \( \left( \frac{I_{\text{ox}}^\infty}{I_{\text{Si}}^\infty} \right) \), and \( \frac{I_{\text{ox}}}{I_{\text{Si}}} \) is the intensity ratio of the measured SiO\(_2\) layer and the Si substrate\(^S1\). In this research, the photoelectron take-off angle \( \theta \) is \( \pi/4 \), \( \lambda_{\text{ox}} \) and \( \beta \) are well-studied constants and refered from Ref. S1. The calculated thickness of the oxide layer is 6.9 Å. This oxide layer is slightly thinner than the native oxide grown in air.

![XPS spectrum of Si 2p](image)

**Figure S1.** X-ray photoelectron spectroscopy of the Si substrate used in the SWNT/Si solar cell.
S2. Performance fluctuation for the solar cells fabricated in different batches

In the experiments, the experimental uncertainties and fluctuations are inevitable. Figure S2 shows more than 200 $J-V$ curves of the fabricated SWNT/Si solar cells. The stable fabrication process and the uniformity of the SWNT film limit the experimental fluctuations in a very low level. The occurrence probability of the low-quality SWNT/Si solar cells is very small (lower than 10%). Such a high reproducibility is very beneficial for the practical applications of the SWNT/Si solar cells.

Figure S2. More than 200 $J-V$ curves of the SWNT/Si solar cell samples fabricated in different batches.
S3. Resonant Raman spectroscopy of the SWNT films

Resonance Raman spectra were measured to characterize and compare the as-synthesized SWNTs and the SWNTs exposed in air for six months. The spectra were measured with a 488 nm excitation laser incident normal to the substrate. The as-synthesized SWNTs have a very high crystallinity with the G/D ratio over 30. After the six-month exposure in air, the intensity of G band of the initial SWNTs was weakened and the peak position of G band was blue-shifted by 2.1 cm\(^{-1}\) from 1590.9 cm\(^{-1}\) to 1593.0 cm\(^{-1}\), while the RBM was also significantly weakened, as shown in the inset of Figure S3 (a) and (b).

Actually, we also found out that other SWNT samples showed the same aging phenomenon. The vertically aligned SWNTs (VA-SWNT) were synthesized by our conventional alcohol catalytic CVD method. As shown in Figure S3 (c) and (d), the intensity of G band was decreased and the shape of the G band slightly changed. Moreover, the G’ (2D) band was also slightly blue-shifted, demonstrating the charge transfer characteristics. The G band would be recovered after anneal in the vacuum.

Our previous Raman study demonstrated that in the SWNTs assembly, there exist a certain amount of suspended individual SWNTs which possess much strong Raman intensity than the rest part of the film.\(^{52,53}\) After exposure in the ambient, the oxygen adsorption to the SWNT film would modify the suspended individual SWNTs and thus suppress the G band intensity. The increase of the absolute D band intensity could not be ensured because the Raman intensity is sensitive to many factors, e.g. different measurement spot and the amount of the measured SWNTs.
Figure S3. (a-b) the RBM, G band and D band of the SWNT films used in this experiment, with the transparency of 60%. (c-d) the RBM, G band, D band and G’ (2D) band of the VA-SWNTs measured right after synthesis and after one-month exposure in air.
S4. Curve fitting of $J-V$ characteristics of SWNT/Si solar cells

Through the curve fitting of the $J-V$ characteristics of the SWNT/Si solar cells measured under dark current, the dark saturation current $I_0$ could be obtained. For an actual $p-n$ diode solar cell, the model of the $J-V$ characteristics under dark condition is given as\cite{S2}

$$I = I_0 \left( \frac{qV}{e^{nkT}} - 1 \right)$$

where $kT/q$ is the thermal voltage which is a constant with the value of 25.85 mV at room temperature; $n$ is the ideality factor; and $I_0$ is the dark saturation current. In this research, this $p-n$ diode equation was utilized to calculate $I_0$. The obtained $I_0$ for the SWNT-Si solar cells using the TCF70, TCF80 and TCF90 films are calculated as $6.35 \times 10^{-10}$ A, $1.44 \times 10^{-10}$ A and $8.47 \times 10^{-10}$ A, respectively.
S5. Spectral response of the SWNT/Si solar cells in the UV and visible light spectrum

Figure S5 gives the spectral responses (SM-250TF, Bunkou Keiki Co. Ltd) of the SWNT-Si solar cells and the reference Si p-n junction solar cell (Si photodiode S1337, Hamamatsu Photonics K.K.). The difference of the spectral response between the Si p-n solar cell and the SWNT/Si solar cells is negligible in the wavelength ranging from 300 nm to 1100 nm. In this wavelength range, the main contribution of photocurrent comes from the Si side in each SWNT/Si solar cell. By integrating the spectral responsivity with the AM1.5G spectrum, the calculated $J_{sc}$ from the incident photon conversion efficiency measurement is 30.3 mA/cm$^2$, calibrated by the reference Si solar cells.

![Figure S5. Spectral responses of the reference Si p-n solar cell as well as the SWNT/Si solar cells with the TCF90 film, TCF80 film and the TCF80 film doped with nitric acid.](image)

**Figure S5.** Spectral responses of the reference Si p-n solar cell as well as the SWNT/Si solar cells with the TCF90 film, TCF80 film and the TCF80 film doped with nitric acid.
Reference


S3. Zhao, P., Einarsson, E., Xiang, R., Murakami, Y., Chiashi, S., Shiomi, J. and Maruyama, S. 